INFLUENCE OF TEMPERATURE ON THE COAGULATION OF SILVER HALIDE SOLS AND OF ARSENIC TRISULFIDE SOL.

By Tominosuke KATSURAI.

Received June 18th, 1932. Published August 28th, 1932.

In a previous paper a short note was given of the coagulation of silver halide sols and of arsenic trisulfide sol which were prepared according to the description of Wo. Ostwald.[1] In this experiment a porcelain beaker was used to contain the sol in heating it in the autoclave. Hydrogen sulfide was not removed from the arsenic sulfide sol used for the experiment.[2]

The present experiment was undertaken with the view to pursue the study in greater detail and to get more exact information as to the nature of coagulation. In heating the sol in an autoclave it is probable that the porcelain itself is affected by the sol above 100°C. and thus the dissolved impurities from the porcelain may cause some change to the coagulation. In order to get rid of this defect a transparent flask of fused quartz with the capacity of 100 c.c. was used in the present experiment. The results of experiments are given in each case.

Experimental.

Silver halide sols. The sols were prepared by mixing of dilute solution of potassium halide with silver nitrate solution, in the following three different proportions, viz.

(1) *In equivalent proportions.* 1 c.c. of 0.1N. potassium halide was diluted to 100 c.c. with water. This diluted solution was poured into 1 c.c. of 0.1N. silver nitrate which had been contained in a beaker.

(2) *Excess of silver nitrate.* 1 c.c. of the potassium halide solution and 2 c.c. of the silver nitrate solution were used.

(3) *Excess of potassium halide.* 2 c.c. of the potassium halide solution and 1 c.c. of the silver nitrate solution were used. The procedures of preparation both in (2) and (3) were same as in (1).

First the coagulation at 100°C. was studied. Test tubes of hard glass were used in this case. The test tubes, each containing the sols,

(1) T. Katsurai, *Sci. Pap. Inst. Phys. Chem. Research.* **12** (1929), 166.
(2) Cf. Wo. Ostwald : Practical Colloid Chemistry, (1926), 6–8.

were heated by the boiling water in a beaker, which was heated from below, and the coagulation taking place thereby was observed.

The three sols, viz. the AgCl-, AgBr- and AgJ-sol of (1) were noticeably turbid as soon as they were prepared indicating that they are unstable. At 100°C. these sols as well as the AgCl-sols of (2) and (3) completely coagulated and settled on the bottom of the test tubes. The sols of other composition viz. the AgBr- and AgJ-sol of (2) and (3) seemed to be very stable against the action of heat, and therefore their coagulation was studied by heating them in an autoclave. The procedure of the autoclave treatment was the same as was described in a previous paper,[1] the only difference being that the flask of quartz was used.

At 120°C. the AgBr- and AgJ-sol of (2) coagulated completely. It was at 180°C. that the AgBr-sol of (3) coagulated completely and settled. The temperature below 180°C. was not sufficient to cause complete coagulation. The AgJ-sol of (3) was the most stable and coagulated almost completely when it was heated at 200°C.

Arsenic trisulfide sol. The sol was prepared by blowing hydrogen sulfide into a solution of arsenious oxide.[2] After the sol formation was complete the excess of hydrogen sulfide was removed by blowing a bubble of air into the sol for half an hour.

The coagulation was studied at 160°, 180° and 200°C. At 160°C. the colour of the sol changed to deep yellow and there was formed some precipitate on the bottom. At 180°C. this tendency predominated. At 200°C. almost of the sol was coagulated and settled on the bottom and the upper part of the sol was almost clear. This is quite different from the sol from which hydrogen sulfide was not removed and which dissolved completely at 180°C. It is suggested that the amount of hydrogen sulfide contained in the sol plays a important rôle in the process of coagulation.

With the intention of testing if there is any difference of light absorption between the two sols (the one from which hydrogen sulfide was not removed, and the other from which hydrogen sulfide was removed by a stream of air) the measurement was carried out within the range of visible light.[3] But there was no noticeable difference between them.

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(1) T. Katsurai, *Sci. Pap. Inst. Phys. Chem. Research*, **13** (1930), 89.
(2) Cf. Wo. Ostwald : loc. cit.
(3) The measurement was carried out by Mr. S. Fukushima.

Summary.

(1) The coagulation of silver halide sols which takes place when they were subjected to heating in an autoclave was studied. It was observed that the sols prepared by using an excess of potassium halide, especially the AgJ-sol in an excess of potassium iodide, were most stable against the action of heat.

(2) The arsenic trisulfide sol from which hydrogen sulfide was removed shows noticeable coagulation at 180° and 200°C. This behaviour is quite different from that of the sol from which hydrogen sulfide was not removed.

(3) The light absorptions of arsenic trisulfide sols, one which is free from hydrogen sulfide and the other containing hydrogen sulfide, were compared. No noticeable difference was observed.

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THE SURFACE TENSIONS OF ETHYL ETHER, ACETONE, TOLUENE AND METHYL ALCOHOL AT LOW TEMPERATURE.

By **Tokuzo TONOMURA** and **Kaoru CHUJO.**

Received June 1st, 1932. Published August 28th, 1932.

The surface tensions of ethyl ether, acetone, toluene and methyl alcohol were measured by means of the capillary rise method. Out of many tubes three capillary tubes, which were considered to have uniform cross sections, were selected, and two marks, say a and b, were etched on them as reference points. The diameters of the capillary tubes were measured with the mercury columns of known weight at point to point, and they were taken against the distances from the reference points a or b as the calibration curves. Each of the capillary tubes, then, was sealed in a tube of about 16 cm. in length and 3 cm. in diameter, as shown in Fig. 1. The tube c was connected to the vacuum loading apparatus which was the same as that in the previous paper.[1]

Fig. 1.

(1) Tonomura and Uehara, this bulletin, **6** (1931), 118.

The materials used for the present experiments were obtained from Kahlbaum pure chemicals and were purified by the ordinary ways. Their boiling points were as follows:

Ethyl ether, 34.28—34.30°C./757.2 mm.; Acetone, 55.98°C./753.4 mm.; Toluene, 109.71—109.80°C./764.9 mm.; Methyl alcohol, 64.89—64.95°C./764.9 mm.

The apparatus sealed off from the loading apparatus was set in the large brass block which was hanged from the ceiling to prevent any disturbances due to the motion of cryostat and others, and to keep vertically. The cryostat and thermometer were the same as those used in the previous experiments.[1]

Table 1.

Surface tensions of ethyl ether.

Temp. °C.	Height. cm.	Radius. cm.	$D^{(2)}-d^{(3)}$	γ (obs.) Dynes/cm.	γ (calc.) Dynes/cm.	Capil.
30.00	1.561	0.02856	0.6982	15.25	15.52	A
,,	2.277	0.01973	,,	15.37	,,	B
25.00	1.609	0.02856	0.7046	15.87	16.11	A
,,	2.359	0.01973	,,	16.07	,,	B
− 1.00	2.694	0.01973	0.7367	19.12	19.24	B
− 18.85	2.926	,,	0.7585	21.46	21.49	B
− 22.48	2.993	,,	0.7616	22.04	21.94	B
− 40.68	2.218	0.02857	0.7821	24.28	24.28	A
− 45.05	3.273	0.01973	0.7869	24.91	24.84	B
− 51.14	3.299	0.02857	0.7936	25.54	25.64	A
− 59.68	2.369	,,	0.8033	26.64	26.78	A
− 63.02	3.501	0.01973	0.8070	27.32	27.23	B
− 70.30	2.454	0.02856	0.8149	27.99	28.21	A
− 72.85	3.612	0.01973	0.8173	28.54	28.54	B
− 80.43	2.552	0.02856	0.8249	29.47	29.56	A
− 85.20	3.744	0.01973	0.8299	30.04	30.14	B
− 93.41	3.852	,,	0.8385	31.23	31.34	B
− 94.75	2.686	0.02856	0.8400	31.58	31.53	A
−108.24	4.026	0.01973	0.8542	33.25	33.42	B

$$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = 2.2261\ (\tau - 8.62)$$

(1) Tonomura and Uehara, this bulletin, **6** (1931), 118.
(2) Keyes and Felsing, *J. Am. Chem. Soc.*, **41** (1919), 589.
(3) Curt Ferdinand Mundel, *Z. physik. Chem.*, **85** (1913), 450.

The height of the meniscus in the capillary tube above the liquid surface together with the mark a or b, were observed by a cathetometer through the transparent part of the cryostat. From the distance between the meniscus and the mark, the diameter of the capillary tube at the position of meniscus was determined with the calibration curve which had been obtained previously. The variation of the diameter due to thermal contraction was neglected, as the expansion coefficient of glass was too small to make appreciable errors in the present experiments.(1)

The experimental results were shown in Table 1, 2, 3 and 4, and diagrammatically shown in Fig. 2 and 3. The surface tensions γ of the

Table 2.

Surface tensions of Acetone.

Temp. °C.	Height. cm.	Radius. cm.	$D^{(2)}-d^{(2)}$	γ (obs.) Dynes/cm.	γ (calc.) Dynes/cm.	Capil.
30.00	1.954	0.02856	0.7797	21.32	21.72	A
,,	2.856	0.01973	,,	21.53	,,	B
20.00	2.045	0.02856	0.7911	22.64	22.98	A
,,	2.979	0.01973	,,	22.79	,,	B
− 1.44	3.288	,,	0.8153	25.92	25.75	B
−14.86	3.431	,,	0.8302	27.54	27.52	B
−18.14	3.495	,,	0.8338	28.17	27.96	B
−25.25	3.551	,,	0.8416	28.89	28.92	B
−35.16	3.690	,,	0.8523	30.41	30.26	B
−36.87	2.567	0.02586	0.8542	30.68	30.50	A
−44.15	3.792	0.01973	0.8620	31.60	31.50	B
−44.88	2.625	0.02586	0.8628	31.69	31.60	A
−57.32	2.716	,,	0.8761	33.30	33.33	A
−66.88	2.798	,,	0.8863	34.71	34.68	A
−75.72	4.150	0.01973	0.8957	35.93	36.07	B
−81.65	2.916	0.02856	0.9019	36.81	36.79	A
−86.41	4.255	0.01973	0.9069	37.30	37.47	B
−91.09	2.989	0.02856	0.9118	38.14	38.15	A

$$\gamma\left(\frac{M}{D}\right)^2 = 1.8516\ (\tau+1.808)$$

(1) The apparatus was constructed by ordinary soda glass, whose expansion coefficient is the order of 10^{-5}.

(2) Felsing and Durban, *J. Am. Chem. Soc.*, **48** (1926), 2885.

liquid in the fifth columns of the tables were calculated with the following formula:

$$\gamma = \frac{1}{2} g r \left(h + \frac{r}{3}\right)(D-d)$$

where r is the diameter of the capillary tube, and g the acceleration due to gravity, that is 980.1 cm./sec.^{2} at Sendai. D and d are the

Table 3.

Surace tensions of toluene.

Temp. °C.	Height. cm.	Radius. cm.	$D^{(1)} - d$.	γ (obs.) Dynes/cm.	γ (calc.) Dynes/cm.	Capil.
20.00	3.362	0.01973	0.8659	28.14	28.12	B
,,	2.681	0.02466	,,	28.05	,,	C
10.50	3.473	0.01973	0.8755	29.40	29.36	B
,,	2.774	0.02466	,,	29.35	,,	C
− 0.00	2.876	0.02466	0.8842	30.72	30.70	C
− 6.33	3.669	0.01973	0.8904	31.59	31.53	B
−10.00	2.967	0.02466	0.8940	32.06	32.02	C
−15.46	3.771	0.01973	0.8994	32.79	32.75	B
− 20.13	3.056	0.02466	0.9039	33.39	33.37	C
−25.73	3.886	0.01973	0.9093	34.16	34.13	B
−30.05	3.136	0.02466	0.9135	34.63	34.71	C
−35.52	4.003	0.01973	0.9187	35.55	35.46	B
−41.07	3.230	0.02466	0.9241	36.08	36.21	C
−44.74	4.103	0.01973	0.9273	36.78	36.71	B
−50.67	3.315	0.02466	0.9332	37.39	37.54	C
−55.10	4.214	0.01973	0.9373	38.18	38.15	B
−60.25	3.398	0.02466	0.9421	38.69	38.86	C
−66.20	4.325	0.01973	0.9476	39.62	39.69	B
−70.30	3.484	0.02466	0.9514	40.06	40.27	C
−76.10	4.451	0.01973	0.9568	41.16	41.09	B
−81.30	3.596	0.02466	0.9615	41.79	41.82	C
−85.85	4.558	0.01973	0.9657	42.54	42.47	B
−92.25	3.704	0.02466	0.9714	43.49	43.38	C
−96.50	4.677	0.01972	0.9753	44.08	43.99	B

$$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = 2.4109\ (\tau - 39.05)$$

(1) Tonomura and Uehara, this bulletin, **6** (1931), 255.

densities of liquid and vapour respectively. The values of D and d used were found in the literatures given in the foot note of the tables. When the values of d were not found in the literatures, they were calculated from the vapour pressure, assuming that the vapour obeys the ideal gas law. The letters in the last columns of the tables represent the capillary tubes used in the measurements.

Table 4.

Surface tensions of methyl alcohol.

Temp. °C	Height. cm.	Radius. cm.	$D-d$[1]	γ (obs.) Dynes/cm.	γ (calc.) Dynes/cm.	Capil.
25.00	2.861	0.01973	0.7882	21.80	21.75	B
,,	2.288	0.02466	,,	21.80	,,	C
15.00	2.945	0.01973	0.7970	22.69	22.70	B
,,	2.354	0.02466	,,	22.67	,,	C
− 0.36	2.456	0.02466	0.8106	24.06	24.04	C
− 5.63	3.131	0.01973	0.8154	24.69	24.57	B
−10.91	2.528	0.02466	0.8205	25.07	25.10	C
−16.54	3.226	0.01973	0.8255	25.75	25.67	B
−20.60	2.600	0.02466	0.8293	26.05	26.09	C
−25.11	3.298	0.01973	0.8334	26.58	26.58	B
−31.78	2.685	0.02466	0.8397	27.24	27.25	C
−34.67	3.383	0.01973	0.8424	27.56	27.56	B
−40.24	2.743	0.02466	0.8476	28.10	28.15	C
−44.00	3.466	0.01973	0.8512	28.53	28.56	B
−49.83	2.811	0.02466	0.8569	29.11	29.19	C
−55.13	3.565	0.01973	0.8619	29.71	29.77	B
−59.42	2.875	0.02466	0.8662	30.10	30.25	C
−66.12	3.671	0.01973	0.8729	30.98	31.00	B
−70.26	2.958	0.02466	0.8770	31.36	31.47	C
−74.66	3.758	0.01973	0.8813	32.02	31.97	B
−80.72	3.038	0.02466	0.8873	32.54	32.67	C
−84.43	3.854	0.01973	0.8911	33.20	33.10	B
−91.27	3.124	0.02466	0.8981	33.91	33.91	C
−94.75	3.970	0.01973	0.9017	34.61	34.32	B

$$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = 560.89 - 1.12481T + 0.000333186T^2$$

(1) Körber, Ann. Physik., (4), **37** (1912), 1012.

liquid in the fifth columns of the tables were calculated with the following formula:

$$\gamma = \frac{1}{2} g\, r \left(h + \frac{r}{3}\right)(D-d)$$

where r is the diameter of the capillary tube, and g the acceleration due to gravity, that is 980.1 cm./sec.^{2} at Sendai. D and d are the

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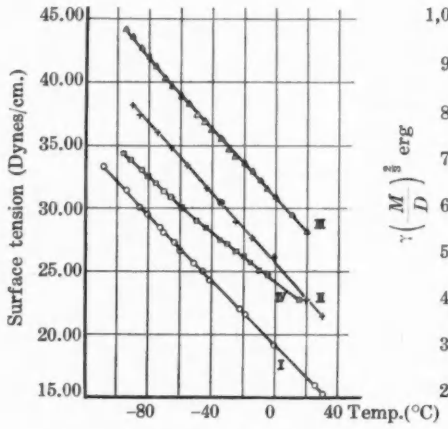
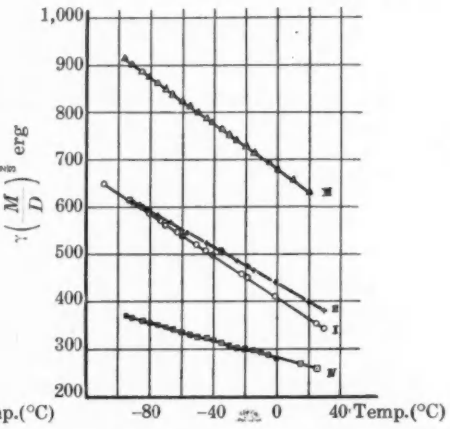


I. Ethyl ether II. Acetone
III. Toluene IV. Methyl alcohol

Fig. 2.



I. Ethyl ether II. Acetone
III. Toluene IV. Methyl alcohol

Fig. 3.

The values of γ in the sixth columns of the tables were calculated from the empirical formula of the Eötvös type given at the end of the tables. They were obtained from the experimental values of γ with the method of the least square. M in those formulae is the molecular weight of the substances and τ is the temperature measured from the critical temperature, which is 194.5°C. for ethyl ether, 235.6°C. for acetone and 320.8°C. for toluene. In the case of methyl alcohol whose molecules were considered to be much associated, the constants suitable for the Eötvös formula were not found and a quadratic formula, therefore, was used, where T is the absolute temperature.

In conclusion, the present authors thank to Prof. S. Mitsukuri for his helpful guidance during their experiments.

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May, 1932.

VAPOUR PRESSURE OF RHENIUM HEPTOXIDE, VAPOUR PRESSURE AND DISSOCIATION PRESSURE OF RHENIUM OCTOXIDE.

By Eijiro OGAWA.

Received June 7th, 1932. Published August 28th, 1932.

As a rule the elements of the 7th group stand in closer relationship to the elements of the 8th group than to those of the 6th group. Rhenium also resembles osmium in many points. For example its oxides, rhenium heptoxide and rhenium octoxide, are volatile without decomposition as is the case in osmium tetroxide, while the oxides of tungsten are not so. In 1929 I. and W. Noddack published their laborious work on these two rhenium oxides. The present author reinvestigated the properties of these substances and found that some of them do not agree with their description. It has been found that rhenium heptoxide does not decompose at its boiling points, 363°C., and so its vapour pressure can be measured. It is true that rhenium octoxide already slightly dissociates into rhenium heptoxide and oxygen at ordinary temperature, but the partial pressure of oxygen is very small even at 220°C., and the vapour pressure of rhenium octoxide can therefore be measured, although accurate values can not be expected.

Experimental Part.

Considering the fact that the result of I. and W. Noddack was obtained by using only one gr. of the metal soon after its discovery, it may be somewhat uncertain. The author found that the results of the preliminary experiments did not well agree with their results as following.

1. The oxides prepared by Noddacks may be not perfectly anhydrous. As rhenium octoxide and heptoxide are both very hygroscopic according to the author's experiments, it would be insufficient to dry the oxygen by merely passing one sulphuric acid bottle, one calcium chloride tube and one phosphorus pentoxide tube as they used in their experiments. Noddacks found that the heptoxide melts at 220°C., a temperature which is very much lower than the author's value, 298°C. This fact indicates that the lower value obtained by them is probably due to the presence of water resulting from insufficient drying of the gas.

(1) I. and W. Noddack. Z. Anorg. Chem. 181, 1-37, (1929).

2. They stated that heptoxide easily changes to octoxide by heating in oxygen. The author found that this is not the case, the reaction $2Re_2O_8 \rightarrow 2Re_2O_7 + O_2$ being almost irreversible.

3. According to Noddacks heptoxide changes to blue lower oxide by heating above 300°C. in a vacuum. It does not, however, decompose at least at its boiling point, 363°C., in the author's experiment.

4. They described in page 11 that crude rhenium heptoxide prepared must be heated in N_2 at 170°C. for 10 minutes in order to convert mixed octoxide to heptoxide. For completing the reaction, however, it has been found desirable to keep in a reduced pressure at 180–190°C. for one or two hours.

5. They stated in page 13 that rhenium heptoxide have a large vapour tension even at 150°C., but the author found its tension at 150°C., was only 3.0 mm.

Vapour Pressure of Rhenium Heptoxide. *Dry of Oxygen.* Oxygen from a bomb was passed into one sulphuric acid washer, two calcium chloride tubes, 3 cm. in diameter and 80 cm. in length, and one empty 2 liter flask and then four phosphorus pentoxide tubes of the same size as the calcium chloride tubes. A spring manometer, one phosphorus pentoxide tube, and four sulphuric acid washers were next connected. All of these connections were made in glass. Velocity of oxygen was 30 c.c. or 40 c.c. per minute.

Apparatus and Preparation. The apparatus was shown in Fig. 1. After cleaning with hot HNO_3 solution of $K_2Cr_2O_7$, the entire system was evacuated to 0.0001 mm. for several hours. The sensibility of this spring manometer was 0.01 mm. 2 Gr. of rhenium was taken into a porcelain boat. At the beginning of heating, a small quantity of Re_2O_8

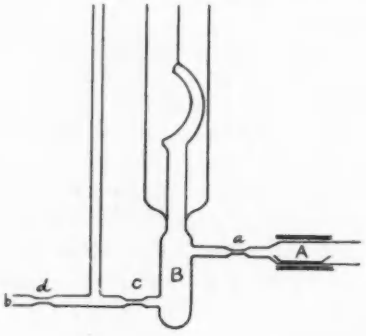

Fig. 1.

was formed, which adhered to the wall of the apparatus, but soon changed to yellow Re_2O_7 on heating with flame. When all of rhenium had sublimated, the apparatus was sealed at a and d. In order to convert octoxide, which might still have remained, into rhenium heptoxide, it was heated at 210°C. for 10 minutes and then at 190°C. for 2 hours, the manometer being immersed in a bath of liquid paraffine and evacuated to 0.0001 mm. It was then sealed at c. The detail of the method of the measurement using a spring manometer was already described in the previously published paper on osmium tetroxide.[2] The electric furnace used for heating was 15 cm. in internal diameter and 50 cm. in depth. It was 13 cm. long from the bottom of B to the top of the spring. The mercury reservoir of the thermometer was placed at the middle of this interval. The temperature fluctuation of the electric furnace was about ±2.0°C. in this interval. Three thermometers were used. Two of these had the range of 100–200°C. and of 200–300°C. respectively, and were graduated into hundredths of a degree. The other had the range of 300–360°C. and was graduated into tenths of a degree. Temperature was so regulated as to be within ±0.3°C. by adjusting the current by hand for about four hours. After each measurement temperature was lowered to the ordinary temperature, and no increase in pressure was observed. This shows that any dissociation did not occur. For reading pressure a cathetometer was used and necessary corrections were added to the data. The data up to 1/10 mm. or

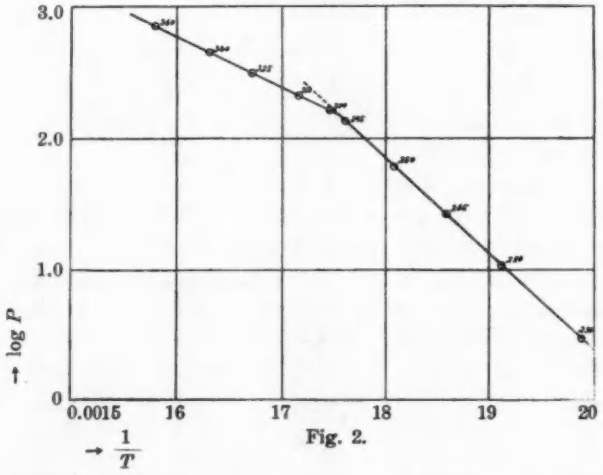

Fig. 2.

(2) This Bulletin, 6 (1931), 302–317.

1 mm. were adopted. Above 340°C. the needle moved a little left or right owing to irregularity of temperature. The vapour pressure soon reached its equilibrium. The relations of $\log P$ and $1/T$ is linear as shown in Fig. 2 and expressed by following August's formulas.

Sublimation:

$$\log P = -7217.95/T + 14.83866.$$

Vaporization:

$$\log P = -3920.13/T + 9.04668.$$

Table 1.

t°C	T°abs.	$1/T$	P mm.	$\log P$
230	503	0.0019881	3.0	0.47712
250	523	0.0019120	10.9	1.03473
265	538	0.0018587	26.5	1.42325
280	553	0.0018083	61.2	1.78675
295	568	0.0017606	135	2.13033
300	573	0.0017452	160	2.20412
310	583	0.0017153	210	2.32222
325	598	0.0016722	312	2.49415
340	613	0.0016313	449	2.65225
360	633	0.0015798	711	2.85187

Melting Point and Boiling Point. The melting point and the boiling point obtained from Fig. 2 are 297°C. and 363°C. respectively. The observed melting point was 297°C.

Heat of Sublimation. The mean heat of sublimation between 230°C. and 295°C. obtained by the above formula is 33050 cal. The mean heats of sublimation in more limited ranges are as follows.

Temperature range	Mean temperature	ΔH (cal.)
230—250	240	33710
250—265	257.5	33140
265—280	272.5	33020
280—295	287.5	32980

Extrapolating to 297°C. we obtain 32910 cal., which is the heat of sublimation at the melting point.

Heat of vaporization. The mean heat of vaporization between 300°C. and 360°C. obtained from the above formula is 17950 cal. The mean heats of vaporization in more limited ranges are as follows.

Temperature range	Mean temperature	ΔH (cal.)
300—310	305	18080
310—325	317.5	18260
325—340	332.5	17700
340—360	350	17750

The heats of vaporization at the melting point and at the boiling point obtained by extrapolation are 18300 cal. and 17400 cal. respectively.

Heat of fusion. 32910–18300 = 14610 cal.

Trouton's constant

$$\Delta H/T = 17400/636 = 27.4$$

According to vapour density measurement of Noddack, rhenium heptoxide has a composition of Re_2O_7 at 502°C.

Vapour Pressure and Dissociation Pressure of Rhenium Octoxide. *Apparatus and Preparation.* Oxygen was dried in the same way as in the case of heptoxide. Velocity of the gas was 100 c.c. or 110 c.c. per minute. The apparatus used was shown in Fig. 3. A, a spiral tube which was made by coiling twelve times a tube of 6 mm. in diameter, was 5.5 cm. in inner diameter and 9 cm. in height. After the apparatus was cleaned carefully, it was dried thoroughly by heating in a vacuum of 0.0001 mm. 2 Gr. of rhenium was taken. At the beginning of the reaction, rhenium octoxide was so rapidly formed that it escaped through four sulphuric acid washers, but with the scintering of the surface of rhenium its production became less and less until rhenium heptoxide began to deposit near the boat. After all of rhenium sublimated, heptoxide was driven into the spiral. Rhenium octoxide, which is white when pure, owing to the presence of rhenium heptoxide, adhered to the inside of the spiral in somewhat yellow fine powder. The apparatus was then sealed at a and b and kept in a vacuum of 0.0001 mm. at ordinary temperature for ten minutes after which it was sealed at c.

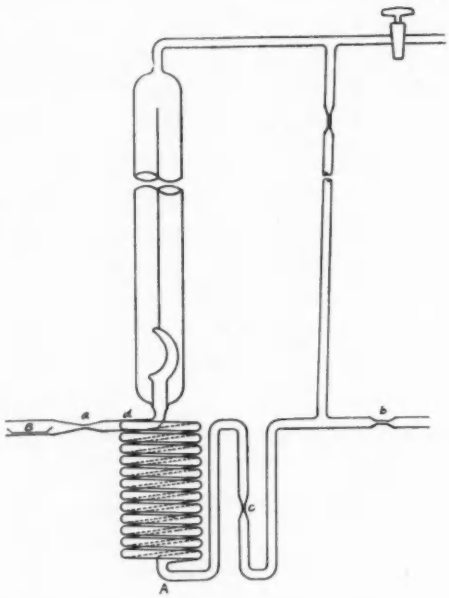

Fig. 3

Dissociation Pressure of Octoxide. For heating, the electric furnace previously described was used. The distance from the bottom of A to the top of the spring was 21 cm. The fluctuation of temperature was ±3°C. On heating at 100°C. pressure rose to 10.8 mm. after about 2 hours from the start and it remained constant for four hours. After cooling it became 3.24 mm. at 14.5°C., which did not change until the next day. The time required to reach the equilibrium pressure became more rapid with rise of temperature. Temperature was maintained constant for four hours in each experiment. Pressure was measured up to 220°C. The results are shown in Table 2. As these increases in pressure did not change during several days, it can be assumed that the reaction $2Re_2O_8 \rightarrow 2Re_2O_7 + O_2$ is perfectly irreversible at ordinary temperature. It was assumed that this increase in pressure indicates the dissociation pressures at each temperature, and the equilibrium pressures were calculated by adding necessary corrections. The values obtained in this manner are shown in the 3rd column in Table 2. The linear relations of $\log P$ and $1/T$ are shown in Fig. 4.

Table 2.

t°C	$1/T$	O_2 press. (mm.)	log P
100	0.0026810	4.19	0.62221
120	25445	4.73	0.67486
140	24213	5.39	0.73159
160	23095	6.01	0.77887
180	22075	6.63	0.82151
200	21142	7.30	0.86332
220	20284	7.84	0.89432

$$\log P = -416.08/T + 1.73877$$

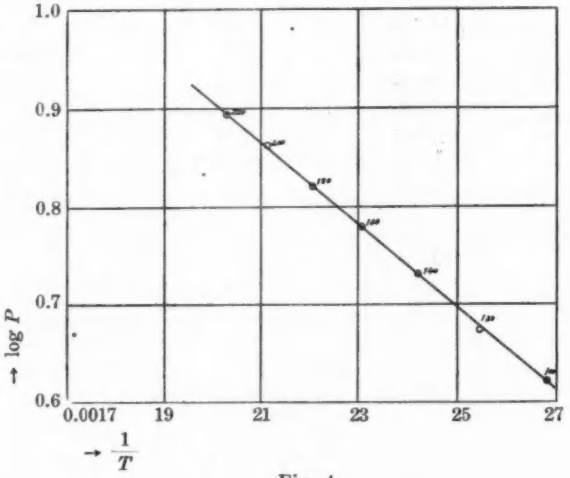

Fig. 4.

Vapour Pressure of Octoxide. The values obtained by substracting the dissociation pressure from the observed pressures were adopted as the vapour pressure of rhenium octoxide as shown in Table 3. In the apparatus used for the determination of dissociation pressure (Fig. 3) the greater part of the heptoxide was in d, and the octoxide, yellowish white in colour due to the presence of a small quantity of heptoxide, was spread all over the spiral. There was nothing in the spring. After heating to 100°C. a small quantity of white sublimate of rhenium octoxide

was observed in the spring. The quantity of this sublimate increased gradually until the temperature at 220°C. and the inside of the spring was covered with it. This pure white sublimate always existed at each temperature of measurement. It shows that there was an excess of octoxide in the spring at each time of the experiment. The reason why rhenium octoxide on cooling should have assembled in the spring may be due to its being surrounded by the outer tube of reduced pressure or inhomogeneity of temperature of the electric furnace. It was unnecessary to consider the influence of rhenium heptoxide, as octoxide was in pure state. The linear relations between the logarithm

Table 3.

t°C	$1/T$	P mm.	log P
100	0.0026810	6.6	0.81954
120	25445	11.7	1.06819
140	24213	18.7	1.27184
160	23095	25.6	1.40824
180	22075	31.8	1.50243
200	21142	39.2	1.59329
220	20284	46.6	1.66839

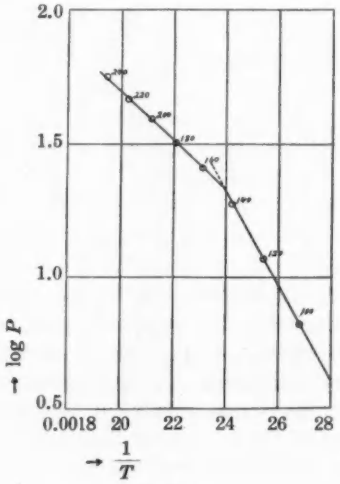

Fig. 5.

of the vapour pressure determined as mentioned above and $1/T$ are shown in Fig. 5. There is a knick at 145°C. It must be the melting point. But this relation can no longer exist above 240°C., owing to the sublimation of heptoxide. As this sublimated heptoxide dissolves in the melted octoxide in the spring it is not possible to calculate the vapour pressure of Re_2O_8.

Sublimation:

$$\log P = -1738.74/T + 5.48512$$

Vaporization:

$$\log P = -924.18/T + 3.54384$$

Heat of Sublimation. The mean heat of sublimation between 100°C. and 140°C. is 7960 cal. Those in more limited ranges are as follows.

Temperature range	Mean temperature	ΔH
100—120	110	8340
100—140	120	7970
120—140	130	7570

Extrapolating to 145°C. 7000 cal. is obtained.

Heat of Vaporization. The mean heat of vaporization between 160° and 220°C. is 4230 cal. Those in more limited temperature ranges are as follows.

Temperature range	Mean temperature	ΔH
160—200	180	4340
180—200	200	4240
160—220	180	4230

The mean heat of vaporization at the melting point obtained by extrapolation is 4500 cal.

Heat of fusion. 7000—4500 = 2500 cal.

Chemical Institute, Faculty of Engineering,
Kyushu Imperial University, Fukuoka.

June, 1932.

STUDIES ON REACTIONS BETWEEN GAS AND SOLID. V. AZOTATION OF CALCIUM CARBIDE AND THE EFFECT OF SIZE OF GRAIN ON ITS VELOCITY.

By Takeo AONO.

Received May 27th, 1932. Published August 28th, 1932.

Experimental.

Experimant A. A block of a technical carbide was crushed by a mill and sieved in three parts: H = (less than 80 mesh), I = (48–80 mesh) and J = (larger than 48 mesh), and H and I were put in reaction with nitrogen in the same reaction tube at 1030°C. for 3 hrs. "Granular carbide"[1] (larger than 48 mesh) added with 5% of calcium fluoride was also subjected to azotation at 1030°C. for 4 hours. Table 5_1 shows the results.

If we assume that the particles are spheres of initial mean radius r_0, which was changed chemically to the depth r', then the ratio of the remaining carbide to the initial is given by Equation (5_1):

Table 5_1.

No. and date of the exp.	Crushed carbide		Granular carbide	
	No. 302 (June 18, 1930)		No. 304 (June 20, 1930)	
	H	I	I	H
Sieves (mesh)	<80	80—48	5—8	8—48
Mean radius (r_0) mm.	0.044	0.117	1.59	0.664
Yield of acetylene (G) c.c./gr. at 15°C.	219.5	264.9	228.0	229.4
Temp. (°C.) and time (hrs.)	1030°; 3	1030°; 3	1030°; 4	1030°; 4
Gr. of samples taken (W)	2.3908	3.3696	2.6606	2.9925
Increase in weight ÷ W = (w)	0.0644	0.0321	0.0602	0.1150
Degrees of azotation %	36.0	12.7	23.6	48.7
Yield of acetylene G c.c./gr.	67.6	189.1	139.5	67.3
$(1+w)G'/G = \alpha$	0.325	0.750	0.650	0.337
α, corrected for efflorescence*	0.413	—	—	—
$1-\sqrt[3]{\alpha}$	0.255	0.091	0.134	0.304
Thickness of reacted layer (r') mm.	0.011	0.011	0.213	0.201

* This correction is due to the change $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$, $Ca(OH)_2 + CaC_2 = 2CaO + C_2H_2$ (by heating) and $C_2H_2 = 2C + H_2$, which has been determined by the author. The numerical value is given by

$$\frac{67.6 \times 1.0644}{219.5 - (264.9 - 219.5)} = 0.413 .$$

(1) Vid. the former paper.

$$a = \frac{(r_0 - r')^3}{r_0^3} = \frac{G'(1+w)}{G}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5_1)$$

$$r' = (1 - \sqrt[3]{a})\, r_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5_2)$$

From these experiments r', namely $\int_0^t \left(\frac{dr'}{dt}\right) dt$, is found to be independent of the initial size r_0 of the particles (at 1030°C.). Whether the value $\left(\frac{dr'}{dt}\right)$ is dependent on time or not is the next problem to be determined, mined.

Experiment B. The method was the same as that of reported in the former papers,[1] the velocity of azotation being determined from time to time by measuring the absorption speed of nitrogen at constant temperature (1140°C.) and pressure (1 atm.). The samples were the "granular" of diameters (0.175–1.0), (1.0–2.0), (2.0–3.0) mm. respectively. The sample of Exp. 376 was (3.17–0.84 mm.) different from others, all being free from catalysers. Table 5_2 and Fig. 1 show the results.

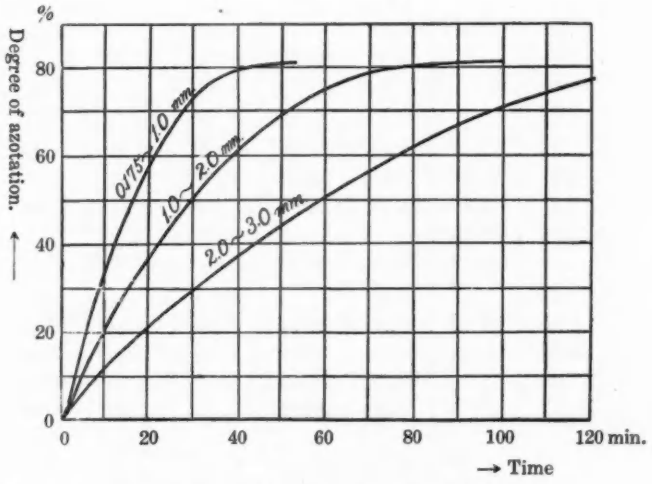

Fig. 1.—Azotation of "granular carbide" of varying size at 1140°C.

(1) This bulletin, **7** (1932), 143.

Table 5_2.

Velocity of azotation of "Granular carbide" of various size at constant temp. (1140°C.) and pressure (1 atm.) of nitrogen (without catalysers).

Exp. No.	389		390		386		376	
Dia. mm.	0.175—1.0		1.0—2.0		2.0—3.0		3.17—0.84	
Purity %	63.9		71.3		72.6		62.9	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	(1.0)	1.18	1.07	1.05	0.578	0.73	1.11	1.70
2	(2.00)	4.86	1.25	3.48	0.695	2.08	1.30	4.08
3	2.00	9.61	1.25	6.10	0.688	3.53	1.35	6.61
4	1.80	14.23	1.19	8.65	0.660	4.94	1.36	9.19
5	1.60	18.26	1.07	10.98	0.623	6.28	1.35	11.75
6	1.47	21.88	1.04	13.17	0.595	7.55	1.33	14.28
7	1.36	25.27	1.00		0.578		1.32	16.78
8	1.30	28.46	1.00	17.36	0.540	9.93	1.29	19.25
9	1.24		0.909		0.525		1.27	21.68
10	1.20	34.38	0.909	21.29	0.525	12.18	1.24	24.05
12	1.11		0.862		0.510		1.18	28.63
14	1.03	45.00	0.833		0.490		1.12	33.02
15	0.99		0.815	30.17	0.475	17.40		
16	0.95		0.769		0.461		1.06	37.40
18	0.885		0.685		0.438		0.995	41.10
20	0.81	58.10	0.699	37.92	0.422	21.99	0.939	44.75
25	0.64	66.60	0.614	44.73	0.390	26.22		
30	0.45	73.30	0.570	50.90	0.370	30.18	0.703	60.02
35	0.265	77.55			0.360	33.98		
40	0.110	79.65	0.440	61.50	0.350	37.66	0.464	71.1
45	0 060		0.377		0.339			
50	0.020	81.00	0.350	69.65	0.325	44.78	0.192	77.0
60	0.000	81.15	0.220	75.30	0.300	51.30	0.064	79.2
70			0.110	78.90	0.270	57.30	0.028	79.9
80			0.047	80.40	0.240	62.65	0,000	80.0
90			0.023	81.10	0.210	67.35		
100			0.000	81.35	0.180	71.35		
120					0.105	77.35		
140					0.042	80.15		
160					0.014	81.10		

If we calculate the values

$$\left\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\right\}/t = k_5 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5_3)$$

where n_t denotes the degree of azotation in % at time t, and n_∞ the final value of n_t, k_5 is found to be nearly constant. (Table 5_3).

Table 5_3.

Velocity constant k_5 for granular carbide at 1140°C.

Exp. No.	389		390		386		376		385	
Dia. mm.	0.18—1		2—1		3—2		3.17—0.84		2—1	
$+C_aF_2$, %	0		0		0		0		4	
Time, min.	n_t	k_5	n_t	k_5	n_t	k_5	n_t	k_5	n_t	k_5
5	18.26	0.0704	10.98	0.0408	6.28	0.0230	11.75	0.044	10.92	0.040
10	34.38	0.0725	21.29	0.0417	12.18	0.0228	24.05	0.048	23.25	0.046
20	58.10	0.0742	37.92	0.0408	21.99	0.0216	44.75	0.051	39.70	0.043
30	73.30	0.0780	50.90	0.0403					53.07	0.043
40	79.65	0.0796	61.50	0.0406	37.06	0.0202	71.1	0.056	64.10	0.043
50	81.00	0.0760	69.65	0.0412					72.35	0.044
60			75.30	0.0418	51.30	0.0204	79.2	0.055	77.70	0.045
70			78.90	0.0426					80.40	0.045
80			80.40	0.0418	62.65	0.0210	80.0	0.056		
90			81.10	0.0410					81.70	0.044
100			81.35	0.0412	71.35	0.0217				
120					77.35	0.0228				
140					80.15	0.0230				
160					81.10	0.0227				
∞	81.15		81.36		81.45		80.0		81.90	
mean k_5		(0.0751)		0.0413		0.0219		0.052		0.0435

Theoretical considerations.

For the velocity of azotation of a spherical carbide grain of an initial mean radius r_0 at a given temperature and pressure, we suppose the following relations:

Case a.

The linear velocity of azotation in the direction of r is constant:

$$-\frac{dr}{dt}=\kappa \quad \cdots\cdots\cdots\cdots \quad (5_a)$$

where r: radius at any time t,
κ: velocity constant.

$$\therefore \quad \kappa=\frac{r_1-r}{t-t_1} \quad \cdots\cdots\cdots\cdots \quad (6_a)$$

If $r_1=r_o$ at $t_1=0$, then

$$\kappa_0=\frac{r_0-r}{t} \quad \cdots\cdots\cdots\cdots \quad (7_a)$$

$$\therefore \quad k_5=\frac{\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\}}{t} \cdots \quad (8_a)$$

Case b.

the linear velocity is inversely proportional to the thickness of the layer of the product:

$$-\frac{dr}{dt}=\frac{\kappa'}{r_0-r} \cdots\cdots\cdots \quad (5_b)$$

$(r_o-r) \propto$ resistance to the proceeding of the reaction.

$$\kappa'=\frac{(r_1-r)\left\{r_0-\frac{1}{2}(r_1+r)\right\}}{t-t_1} \quad (6_b)$$

$$\kappa_0'=\frac{(r_0-r)^2}{t} \quad \cdots\cdots\cdots \quad (7_b)$$

$$\therefore \quad k_5'=\frac{\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\}^2}{t} \quad (8_b)$$

because $r=\nu m^{\frac{1}{3}}=\mu(n_\infty-n_t)^{\frac{1}{3}}$ and $r_0=\nu m_0^{\frac{1}{3}}=\mu n_\infty^{\frac{1}{3}}$; m: mass of a grain; n_∞, n_t: degree of nitrogen-fixation, and ν, μ: constants.

From the experimental results, shown in Table 5_3., we see that at temperature of 1140°C. k_5 are almost constant at any time after $t=10$ minutes from the beginning. Hence, in case of the "granular carbide," the linear velocity of azotation of the carbide towards the center is constant at 1140°C. If we denote the mass of a carbide granule with m, the reactive surface with A, and the density with δ, then from Equation (5_a) we have:

$$-\frac{dm}{dt}=-A\cdot\delta\cdot\frac{dr}{dt}=\kappa\cdot A\cdot\delta\,, \quad \cdots\cdots\cdots\cdots \quad (9_a)$$

and also $$-\frac{dm}{mdt}=-\frac{d\ln m}{dt}=\kappa\cdot F\cdot\delta\,, \quad \cdots\cdots\cdots\cdots \quad (10_a)$$

where $F=A/m=$ specific surface of the remaining carbide. Hence, the rate of change of the carbide to cyanamide at these higher tem-

peratures and under a constant pressure is proportional to the surface area.

It was already pointed out in the former paper[1] that at temperatures lower than 950°C. and in case of powdered carbide without effective catalysers, the following relation holds good:

$$n_t = n_\infty - \left\{n_\infty^{\frac{1}{3}} - \sqrt{k_5'(t-t')}\right\}^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4_8)$$

or

$$\frac{\{n_\infty^{\frac{1}{3}} - (n_\infty - n_t)^{\frac{1}{3}}\}^2}{t-t'} = k_5' = \text{constant} \quad \ldots\ldots\ldots\ldots\ldots \quad (4_7)$$

This equation coinsides with (8_b), although it has a term $(t\text{-}t')$ instead of t. This t' is a correction due to the initial disturbance of the velocity, which starts with very low values, and attains a maximum after several minutes. This shows that at temperatures lower than about 950°C., the layer of the products hinders the further progress of the reaction proportionally to the thickness of the layer.

At temperatures, where the products melt partly with the carbide, or when some catalysers such as $CaCl_2$ were added, the relation is of course different from the above. (See the former papers.[1]).

Even at moderate temperatures, it is sometimes found that a velocity-curve at constant pressure involves several fragments of different nature: starting from an initial acceleration- or induction-curve, it passes a maximum point and then describes either a constant linear velocity curve or a curve of the first order and turns finally to a parabolic curve.

These experiments were carried out in the research laboratory of the Denki-Kagaku-Kogyo Co. Ltd., Tokyo, before Sept. 10th (1930), and reported to the meeting of the directors and engineers of the Co. on that day.

Summary.

The effect of size of powder and grain of carbide on the velocity of azotation was experimentally discussed, and it was also experimentally determined that the velocity of azotation of carbide at constant temperature and pressure is

1. proportional to the surface area of individual grains, in case of the "granular" carbide, and the radial velocity of azotation is constant at about 1140°C. or

(1) Aono, loc. cit.

2. the radial velocity is inversely proportional to the thickness of changed layer at 950°C. and lower temperatures.

3. In some cases, there are several types of character in the velocity.

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THE INTERFACIAL TENSIONS BETWEEN HEXANE AND AQUEOUS SALT SOLUTIONS.

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The interfacial tension between two liquids is affected, in general, more or less by a third component which is added to this system. In the system of water and hydrocarbon oil each component has actually no mutual solubility and the added inorganic salt is only soluble in the water phase. Therefore the change of the interfacial tension caused by the concentration change of the salt solution should run parallel to that of the surface tension of the salt solution.

But an unexpected result was obtained in the experiment of McLewis on the interfacial tension of hydrocarbon oil against aqueous solution of metallic salt, namely the lowering of the interfacial tension occurred by the addition of $CuCl_2$, $AgNO_1$, or KCl.[1] Since each of these substances raises the surface tension of water against air, and does not influence that of the organic liquid, so that the interfacial tension might be expected to be raised.

As McLewis used a dynamical method, while the present experiment was undertaken in order to repeat it statically.

Experimental.

Material. "Normal hexane from petroleum" from Kahlbaum has been used after distillation, the boiling point of which being 68.5°C. and the density 0.6691.

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(1) McLewis, *Phil. Mag.*, (6) **17** (1909), 466.

Surface Tension of Aqueous Salt Solution. Ordinary capillary rise method was used, and the capillary rise was read by means of a cathetometer. Calculations were made by the following formula.

$$a = \frac{1}{2} r g h (d - d')$$

where a denotes the surface tension, r radius of the capillary, g gravity constant, h capillary rise, d density of the liquid and d' density of the air.

Meniscus correction for the reading of h was neglected considering the accuracy of the present experiment. For the density of air 0.0012 (at 20°C. under 760 mm. Hg) was taken into calculation. The results are shown in Table 1.

Table 1. at 20°C.

Solute	C (gram-mol per litre)	d	$r = 0.0415$ cm. h (cm.)	a (dyne/cm.)
$BaCl_2$	0	0.9982	3.535	71.7
,,	0.01	1.0000	3.525	71.8
,,	0.05	1.0074	3.510	72.0
,,	0.1	1.0162	3.495	72.2
,,	0.3	1.0532	3.400	72.8
$BaBr_2$	0.01	1.0008	3.530	71.8
,,	0.05	0.0112	3.510	72.0
,,	0.1	1.0241	3.410	72.2
,,	0.3	1.0842	3.335	72.8
NaCl	0.01	0.9986	3.535	71.8
,,	0.05	1.0003	3.535	71.9
,,	0.1	1.0024	2.530	72.0
,,	0.3	1.0095	3.520	72.2
,,	0.4	1.0146	3.515	72.5
KCl	0.01	0.9985	3.535	71.8
,,	0.05	1.0008	3.535	71.9
,,	0.1	1.0030	3.530	72.0
,,	0.2	1.0075	3.515	72.1
,,	0.3	1.0122	3.505	72.2
KBr	0.01	0.9991	3.535	71.8
,,	0.05	1.0039	3.530	71.9
,,	0.1	1.0067	3.515	72.0
,,	0.2	1.0150	3.495	72.1
,,	0.3	1.0233	3.460	72.2

Table 1.—(*Concluded*)

Solute	$C\left(\frac{\text{gram-mol}}{\text{per litre}}\right)$	d	$r = 0.0415$ cm. h (cm.)	α (dyne/cm.)
KI	0.01	0.9985	3.535	71.8
,,	0.05	1.0043	3.525	71.9
,,	0.1	1.0104	3.505	72.0
,,	0.3	1.0345	3.440	72.2
$CuCl_2$	0.01	0.9994	3.530	71.8
,,	0.05	1.0043	3.515	72.0
,,	0.1	1.0100	3.515	72.2
,,	0.2	1.0222	3.480	72.4
,,	0.3	1.0343	3.469	72.8
$AgNO_3$	0.01	0.9995	3.535	71.8
,,	0.05	1.0053	3.525	72.0
,,	0.1	1.0120	3.505	72.2
,,	0.3	1.0401	3.420	72.4
$Ba(NO_3)_2$	0.01	1.0004	3.530	71.8
,,	0.05	1.0090	3.510	72.0
,,	0.1	1.0195	3.485	72.2
,,	0.2	1.0395	3.425	72.4
$[Co(NH_3)_6]Cl_3$	0.01	0.9995	3.530	71.8
,,	0.05	1.0046	3.520	72.0
,,	0.1	1.0106	3.510	72.1
,,	0.2	1.0232	3.485	72.2

Some of the above data are protted on curves in Fig. 1.

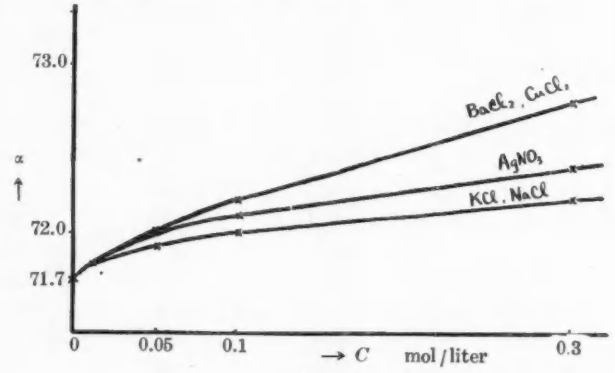

Fig. 1.

The Interfacial Tension. Determinations of the interfacial tensions were made by F. E. Bartell and F. L. Miller's method.[1] The apparatus used is shown in Fig. 2. One of the advantages of this apparatus is that the diameter of the capillary need not be stictly uniform throughout. Calibration of the capillary is necessary only for a given point. It consists of two cups A and B, about 4 cm. in diameter and 10 cm. in height, and these are connected with a U-tube, one arm of which is a capillary of 0.0385 cm. radius.

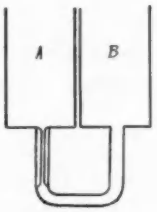

Fig. 2.

The aqueous solution is put into the cup B filling the U-tube. Then oil hexane is introduced into the cup A so that an interface is formed at the top of the capillary. More oil is added drop by drop until the interfacial meniscus is forced back just to the calibrated point. The heights of the liquid in A and B respectively, above the meniscus of the oil, say h and h', are read by means of a cathetometer. The following condition must be fulfiled in equilibrium.

$$\pi r^2 h d g = \pi r^2 h' d' g + 2\pi a r$$

where d and d' denote the densities of the liquid in A and B respectively, a the interfacial tension, r the radius of the capillary and g the gravity constant. Therefore

$$a = {}^1/_2 r g (h d - h' d')$$

The results of the experiment are given in Table 2 and also shown by curves in Fig. 3.

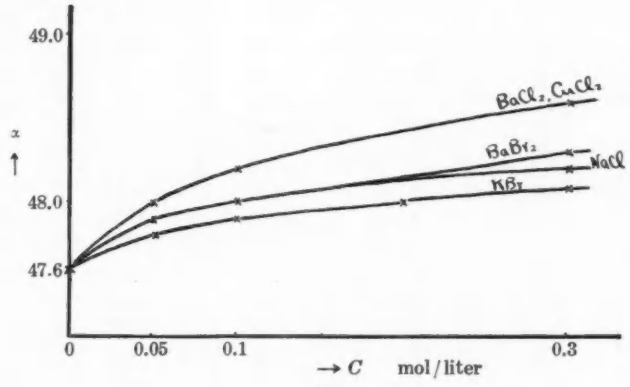

Fig. 3.

(1) F. E Bartell and F. L. Miller, *J. Am. Chem. Soc.*, **50** (1928), 1961.

Table 2.

Solute	$C\left(\frac{\text{gram-mol}}{\text{per litre}}\right)$	h (cm.)	h' (cm.)	$h\,d-h'\,d'$	α (dyne/cm.)
$BaCl_2$	0	10.290	4.355	2.539	47.6
,,	0.05	9.350	3.670	2.559	48.0
,,	0.1	9.070	3.445	2.567	48.2
,,	0.3	8.885	3.180	2.590	48.6
$BaBr_2$	0.01	8.807	3.345	2.545	47.8
,,	0.05	8.510	3.115	2.549	47.9
,,	0.1	8.290	2.290	2.557	48.0
,,	0.3	8.810	3.090	2.572	48.3
NaCl	0.05	7.905	2.735	2.552	47.9
,,	0.1	8.615	3.195	2.558	48.0
,,	0.3	9.370	3.670	2.566	48.2
,,	0.4	8.615	3.145	2.573	48.3
KCl	0.05	8.855	3.370	2.554	47.9
,,	0.1	10.080	4.170	2.559	48.0
,,	0.2	9.632	3.855	2.561	48.1
,,	0.3	9.775	3.915	2.566	48.2
KBr	0.05	8.885	3.410	2.545	47.8
,,	0.1	9.175	3.665	2.551	47.9
,,	0.2	7.665	2.525	2.559	48.0
,,	0.3	8.990	3.375	2.561	48.1
KI	0.05	8.795	3.330	2.541	47.7
,,	0.1	9.375	3.690	2.543	47.8
,,	0.3	8.925	3.300	2.558	48.0
$CuCl_2$	0.05	8.560	3.155	2.559	48.0
,,	0.1	9.645	3.850	2.568	48.2
,,	0.2	8.930	3.335	2.570	48.3
,,	0.3	8.685	3.115	2.589	48.6
$Ba(NO_3)_2$	0.05	8.425	3.055	2.555	48.0
,,	0.1	9.270	3.570	2.564	48.2
,,	0.2	9.720	3.785	2.572	48.3
$AgNO_3$	0.05	8.525	3.140	2.548	47.9
,,	0.1	9.515	3.655	2.554	48.0
,,	0.3	9.185	3.445	2.566	48.2
$Co(NH_3)_6Cl_3$	0.05	9.490	3.790	2.543	47.8
,,	0.1	8.630	3.185	2.556	48.0
,,	0.2	9.010	3.385	2.566	48.2

As we see from the table, the results indicate that, on the contrary to that of McLewis, the interfacial tension of aqueous salt solutions against hexane increase by the increase in concentration of the former, and that the interfacial tension runs approximately parallel to that of the surface tension of the salt solution against air.

Dynamical Measurement of the Interfacial Tension. Drop number method was also tried for the measurement of the interfacial tension to compare the results with that of the statical method. Results obtained by two types of dropping pipette coincided to each other and nearly coincided to that obtained by statical method as shown in Table 3. Calculations were made by the following formula.

$$a = a_0 \frac{n_\omega(d-d_0)}{n(d_\omega-d_0)}$$

where a_0: interfacial tension between water and hexane; n_ω: drop number of water in hexane; n: drop number of solution in hexane; d_ω: density of water; d: density of solution; d_0: density of hexane.

Table 3.

Solute	C (gram-mol per litre)	n	a (dynamical)	a (statical)
$BaCl_2$	0	294	47.6	47.6
,,	0.05	301	47.8	48.0
,,	0.1	309	48.0	48.2
,,	0.3	338	48.4	48.6
$BaBr_2$	0.05	303	47.7	47.9
,,	0.1	317	47.9	48.0
,,	0.3	359	48.2	48.3
$CuCl_2$	0.05	297	47.7	48.0
,,	0.1	302	47.9	48.2
,,	0.3	325	48.2	48.6
NaCl	0.1	297	47.8	48.0
,,	0.4	305	48.1	48.3
KBr	0.2	306	47.8	48.0
,,	0.3	316	48.0	48.1

The writer wishes to thank Professor J. Sameshima, under whose kind suggestion this work was carried out.

Summary.

The interfacial tensions between aqueous inorganic salt solutions and hexane have been measured by both statical and dynamical method. Results indicate that the interfacial tensions increase by the increase in concentration of the salt solutions, being nearly parallel to the surface tension of the salt solutions.

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